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## PATENT ABSTRACTS OF JAPAN

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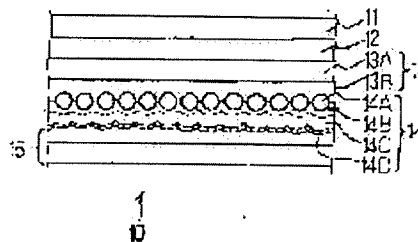
## (54) RETROREFLECTION SHEET HAVING GOOD VISIBILITY

(57)Abstract:

PURPOSE: To provide the retroreflection sheet which is sufficiently visible even in the daytime by providing at least one surface of a retroreflective element with a transparent fluorescent colored layer thereon.

CONSTITUTION: The transparent fluorescent colored layer 12 is formed by coating a polyethylene terephthalate film 11 with a transparent fluorescent colored coating material. A transparent colored coating material is applied on the transparent fluorescent colored layer 12 to form a transparent colored layer 13A and a transparent colored coating material is applied on this transparent colored layer 13A to form a bead stuck layer 13B. Beads 14A are stuck to the bead stuck layer 13B. Focus layers 14B and 14C consisting of art acrylic resin and others are then successively formed thereon and aluminum is deposited by evaporation on the focus layer 14C, by which a light reflection film 14D is formed.

The retroreflective element 14 is constituted of the beads 14A, the focus layers 14B and 14C and the light reflection film 14D. A laminated sheet having the film 11, the transparent fluorescent colored layer 12, the transparent colored layer 13 consisting of the transparent colored layer 13A and the bead stuck layer 12B and the retroreflective element 14 is laminated on a base material sheet 15.



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- 3.In the drawings, any words are not translated.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention relates to the retroreflection sheet with sufficient visibility suitably used as safe materials, such as number plates, such as a road sign, a car, and a motorcycle, or a car, and clothes, etc.

[0002]

[Description of the Prior Art]This kind of retroreflection sheet is well known from the former by combining a reflective element and a coloring layer as a sheet in which day and night demonstrate visibility fair. Usually the above-mentioned reflective element combines a spherical lens and a light reflection film, is constituted, carries out retroreflection of the light which entered into the retroreflection sheet, and enables it to recognize it visually.

[0003]

[Problem to be solved by the invention]However, although the conventional retroreflection sheet can acquire sufficient visibility at night, SUBJECT that the visibility of daytime is not enough, an advertisement and the signs for advertisement were buried into these signs, and various sorts and the distinguishing mark made from the retroreflection sheet when it was installed in large quantities and intermingled made the visibility in daytime difficult increasingly like these days especially in the road etc. occurred.

[0004]Therefore, the purpose of this invention can fully be recognized visually daytime also, and it has high retroreflective properties collectively, and there is in providing the retroreflection sheet which can fully be recognized visually also at night.

[0005]

[Means for solving problem]In a retroreflection sheet which has a reflective element, if this invention provides a retroreflection sheet having a transparent fluorescence coloring layer on at least one surface of a reflective element, it will be boiled, and it attains the above-mentioned

purpose more.

[0006]Hereafter, this invention is explained. A retroreflection sheet of this invention has a reflective element. As for especially this reflective element, although it is not restricted, if productivity, cost, etc. are taken into consideration, what has a light reflection film which consists of spherical glass, i.e., a glass bead, and light reflex nature materials, such as aluminum formed by vacuum evaporation etc., is preferred. And as such a reflective element, a publicly known thing can be used from the former.

[0007]A transparent fluorescence coloring layer on at least one surface of the above-mentioned reflective element is formed with transparent resin containing fluorescent colorant. Therefore, this transparent fluorescence coloring layer may be formed in both sides of the above-mentioned reflective element.

[0008]And although what is necessary is for this transparent fluorescence coloring layer to penetrate incident light, and just to have sufficient total light transmittance to penetrate and emit a reflected light in the above-mentioned reflective element and this total light transmittance changes also with colors of fluorescent colorant, Usually, 50 to 90% is preferred, 60 to 85% is more preferred, and 65 to 80% is still more preferred. At less than 50%, transmissivity of light has too low total light transmittance, if a reflected light from a reflective element is almost lost and total light transmittance exceeds 90% conversely, coloring nature as a transparent fluorescence coloring layer is not enough, and a reflected light with vivid visibility cannot be obtained. Although it is not restricted, if productivity, cost, etc. are taken into consideration, as for especially this transparent fluorescence coloring layer thickness, 15-35 micrometers is preferred, and its 18-28 micrometers are usually more preferred. Although not restricted especially as the above-mentioned fluorescent colorant, perylene system fluorescent colorant, Naphthol imide system fluorescent colorant, SHIAMINO stilbene series fluorescent colorant, Although what is necessary is just to use fluorene series fluorescent colorant, thioflavine system fluorescent colorant, eosine system fluorescent colorant, rhodamine fluorescent colorant, etc., perylene system fluorescent colorant and naphthol imide system fluorescent colorant which are excellent in weatherability are preferred, and it is most preferred to use perylene system fluorescent colorant especially. And 0.1 to 5% of content of this fluorescent colorant is desirable, is more desirable, and is still more desirable. [ 0.2 to 1.5% of ] [ 0.1 to 2% of ] Although it is not restricted, if weatherability, film production nature, etc. are taken into consideration, especially resin that forms the above-mentioned transparent fluorescence coloring layer has acrylic resin, polyester system resin, polyvinyl-chloride system resin, urethane system resin, preferred fluororesin, etc., and its acrylic resin is especially more preferred, for example. In this transparent fluorescence coloring layer, an additive agent which the usual resin films, such as light stabilizer and an anti-oxidant, are made to contain can be added suitably.

[0009]A retroreflection sheet of this invention has that preferred to which a transparent coloring layer intervened between at least one surface of the above-mentioned reflective element, and the above-mentioned transparent fluorescence coloring layer. Thus, a transparent coloring layer is added in a layer transparent fluorescence coloring layer independent [ above-mentioned ] because coloring performance of fluorescent colorant is weak and sufficient coloring nature is difficult to get. Although content of fluorescent colorant in a transparent fluorescence coloring layer can be raised and coloring of this layer can also be raised to be sure, if it does in this way, it becomes a cost hike and is not desirable on quality of a retroreflection sheet. In addition, the weatherability of a retroreflection sheet can also be raised by making a transparent coloring layer intervene between at least one surface of a reflective element, and a transparent fluorescence coloring layer. Namely, if a transparent fluorescence coloring layer and a transparent coloring layer are made into similar colors. For example, by hue of a transparent coloring layer, even if a transparent fluorescence coloring layer using fluorescent colorant generally said for weatherability to be weak compared with usual colorant was faded by an outdoor use over a long period of time, as a color seldom changed in visual appreciation, it can show. What is necessary is to \*\*, and for this transparent coloring layer to penetrate incident light like the above-mentioned transparent fluorescence coloring layer, and just to have sufficient total light transmittance to penetrate retroreflection light in a reflective element, From the same Reason as the above-mentioned transparent fluorescence coloring layer, usually 30 to 85% of this total light transmittance is desirable, is more desirable, and is still more desirable. [ 50 to 70% of ] [ 40 to 80% of ] Although it is not restricted, if productivity, cost, etc. are taken into consideration, as for especially this transparent coloring layer thickness, 15-30 micrometers is preferred, and its 20-25 micrometers are usually more preferred. Although not restricted especially as the above-mentioned colorant, if weatherability and transparency are taken into consideration, For example, a quinacridone series, a perylene system, a flavan SURON system, an isoindolinone system, condensation azo, a cyanine system, a DPP system, etc. are preferred, and a quinacridone series, an isoIndia Sorin system, a cyanine system, a DPP system, and a flavan SURON system are especially preferred. And 0.1 to 5% of content of this colorant is desirable, is more desirable, and is still more desirable. [ 0.2 to 1.5% of ] [ 0.15 to 2% of ] Although it is not restricted, if weatherability, film production nature, etc. are taken into consideration, especially resin that forms the above-mentioned transparent coloring layer has acrylic resin, polyester system resin, polyvinyl-chloride system resin, urethane system resin, preferred fluororesin, etc., and its acrylic resin is especially more preferred, for example. In this transparent coloring layer, fluorescent colorant can be further added for an additive agent which the usual resin films, such as light stabilizer and an anti-oxidant, are made to contain suitably depending on the case. Although there is also a method of making the same hyaline layer mix and contain fluorescent colorant and

colorant, in this case, it can be hard to employ vividness of fluorescent colorant efficiently, and is not desirable.

[0010]By combining a transparent fluorescence coloring layer and a transparent coloring layer as mentioned above, in a transparent fluorescence coloring layer. Predetermined wavelength light is reflected with the fluorescent colorant, and wavelength of a reflected light from a layer which collaborates with a transparent coloring layer located in a lower layer, and has a reflective element is controlled to the transmitted light of predetermined wavelength, and these both light can lap and it can control in a very skillful light.

[0011]Chroma saturation is made to a very high thing with combination with a transparent fluorescence coloring layer, a transparent coloring layer, and a reflective element, with high retroreflective properties held. In order to acquire visibility which was excellent in daytime, as for chroma saturation, 50 or more are preferred, and 60 or more are more preferred.

[0012]Although a manufacturing method in particular of a retroreflection sheet of this invention is not limited, its laminated layers method according to casting at points, such as accuracy of thickness of each layer and each smooth nature, is preferred.

[0013]

[Function]When light enters into a retroreflection sheet according to this invention, the reflected light in a transparent fluorescence coloring layer and a transparent coloring layer, While the light which penetrated the transparent fluorescence coloring layer and the transparent coloring layer, was attained and reflected in the reflective element and penetrated the transparent coloring layer and the transparent fluorescence coloring layer again is put together and offering a desired color, a very skillful light is emitted.

[0014]

[Working example]Hereafter, each embodiment of this invention is described, referring to drawing 1. Drawing 1 is a figure expanding and showing the section of one embodiment of the retroreflection sheet of this invention.

[0015]Before explaining this example and a comparative example, the measuring method of total light transmittance performed to these, the measuring method of the thickness of each layer, and the measuring method of a colorimetry value are explained first.

[0016](\*\*) The value obtained by measuring total light transmittance using what carried out lamination fixing of a total-light-transmittance transparent fluorescence coloring layer and the transparent coloring layer to one side of polyethylene terephthalate (PET) of 88.5% of total light transmittance respectively was <sup>(ed)</sup> by 0.885, and the transmissivity of each layer was measured. Each measurement was performed based on the color-of-object measuring method of JIS Z 8722. Measuring equipment used SC-2-CH made from SUGA Tester.

(\*\*) In the case of a thickness transparent fluorescence coloring layer, thickness produced a 20x200-mm sample using what carried out lamination fixing of the transparent fluorescence

coloring layer at one side of known PET. And thickness was measured about ten points at an interval with an equal abbreviation using a dial gage specified to JIS B7509 about the length direction of this sample, transparent fluorescence coloring layer thickness was computed by having deducted thickness of PET, and average value of measured value of ten points was adopted as transparent fluorescence coloring layer thickness. It asked for the thickness similarly about a transparent coloring layer.

(\*\*) Based on a measuring method of a color in which it is specified JIS Z-9117, the colorimetry of the retroreflection sheet which carried out colorimetry value completion was carried out. However, as for a light source, a color system used a hunter system (L, a, b) using standard illuminant C.

(\*\*) Based on a colorimetry value which carried out the colorimetry, it asked for chroma saturation of a retroreflection sheet with the following numerical orientation method by chroma saturation (\*\*).

Chroma saturation =  $\sqrt{a^2 + b^2}$  [0017] It \*\* (ed) and a visibility examination of a sample obtained in each embodiment was done as follows. That is, a sample 10 cm in length and 4.5 cm in width is produced from each invention, and a reflective sheet of the conventional orange of 20 cm in length and 25 cm in width a white and black reflective sheet which does not contain each invention and fluorescent colorant in the center section is mostly fixed at intervals of 4.5 cm. A sheet which fixed this sample is installed in height about 150 cm above ground. A sample where eyesight wears a person of 0.7, and glasses by the naked eye applying a person of 0.3 by the naked eye and which has eyesight in height about 150 cm above ground by three of persons of 1.5 in and a 50-m-away position and a 100-m-away position. A quality of a sample was judged by whether under a daylight illuminant, I have you recognize visually, respectively and each sample can be recognized visually. And each visual recognition result was shown in Table 1.

[0018] In embodiment 1. this example, first, in the procedure of following A-C, produce the lamination layer sheet which has the transparent fluorescence coloring layer 12, the transparent coloring layer 13, and the reflective element 14 which are shown in drawing 1, and it ranks second, After producing the base material sheet 15 which supports this lamination layer sheet in the procedure of the following D, the retroreflection sheet 10 was produced by laminating the above-mentioned lamination layer sheet to this base material sheet 15.

Formation (1) acrylic resin (Tokushu Shikiryō Color & Chemicals [ , INC. ] make: trade name ST-100) of preparation of a transparent fluorescence coloring paint, and the transparent fluorescence coloring layer 12 A. 200 weight sections, Red perylene system fluorescent colorant (BASF [ A.G. ] make: trade name RUMOGEN F red 300) 0.21 weight sections, Using the homomixer, at the number of rotations of 4000 rpm, stirring mixing was carried out for 20 minutes, and MEK(methyl ethyl ketone)5 weight section and MIBK(methyl isobutyl ketone)5

weight section were prepared as fluorescence red \*\*.

(2) Stirring mixing of the 0.5 weight sections was carried out for 20 minutes at the number of rotations of 4000 rpm using the homomixer, and the acrylic resin 100 above-mentioned weight section and orange perylene system fluorescent colorant (BASF [ A.G. ] make: trade name RUMOGEN F orange 240) were prepared as fluorescence orange \*\*.

Fluorescent colorant of the above-mentioned orange to 100 weight sections for the above-mentioned acrylic resin (3) 0.21 weight sections, MEK(methyl ethyl ketone)5 weight section and MIBK(methyl isobutyl ketone)5 weight section were added, respectively, using a homomixer, at number of rotations of 4000 rpm, stirring mixing was carried out for 20 minutes, and this was prepared as fluorescence orange \*\*.

Rank second and 72.4 weight sections and fluorescence orange \*\* for fluorescence red \*\* (4) 70 weight sections, A melamine cross-linking agent (made in Sanwa Chemical: trade name NIKARAKKU MS-11) 27.1 weight sections, 7.1 weight sections and an ultraviolet ray absorbent (made in SHIPRO Chemicals: trade name SHISOPU 103) were carried out for a catalyst, stirring mixing of the 33.4 weight sections was carried out for 0.7 weight sections and MIBK, and it prepared as a transparent fluorescence coloring paint. And this transparent fluorescence coloring paint was applied to PET film 11, and it formed as the 25-26-micrometer transparent fluorescence coloring layer 12. The above-mentioned catalyst is what diluted :BEKKAMIN P-198 (trade name) by Dainippon Ink & Chemicals, Inc. with a solution of a rate of BEKKAMIN P-198:toluene:IPA=5:70:25, and sets this catalyst to CT-5.

[0019]Formation (1) acrylic resin (Tokushu Shikiryō Color & Chemicals [, INC. ] make: trade name ST-230) of preparation of a transparent coloring paint, and the transparent coloring layer 13 B. 100 weight sections, The transparent colorant 1 (Tokushu Shikiryō Color & Chemicals [, INC. ] make: trade name HFG base) 3.9 weight sections, The transparent colorant 2 (Tokushu Shikiryō Color & Chemicals [, INC. ] make: trade name AR-860 an orange) 7.1 weight sections, The transparent colorant 3 (Tokushu Shikiryō Color & Chemicals [, INC. ] make: trade name AR-N7200 orange) 5.0 weight sections, 0.5 weight section and melamine cross-linking agent NIKARAKKU MS-11 was carried out for 3.1 weight sections and ultraviolet ray absorbent SHISOPU 103, stirring mixing of the 8.6 weight sections was carried out for 10.5 weight sections and MIBK, and the transparent colorant 4 (Tokushu Shikiryō Color & Chemicals [, INC. ] make: goods name AR-N4200 yellow) was prepared as a transparent coloring paint. And this transparent coloring paint was applied on the above-mentioned transparent fluorescence coloring layer, and the 20-21-micrometer transparent coloring layer 13A was formed.

Acrylic resin (Tokushu Shikiryō Color & Chemicals [, INC. ] make: trade name ST-300) (2) 100 weight sections, The transparent colorant 5 (Tokushu Shikiryō Color & Chemicals [, INC. ] make: trade name AR-7300 an orange) 0.4 weight sections, 16.4 weight sections were carried



out for MIBK, 12 weight sections improved 16 weight sections and an isocyanate cross-linking agent (a product made from Sumitomo Beyer Urethane: trade name SUMIDULE N-75) stirring mixing of SS1500 (Mitsubishi Oil [ Co., Ltd. ] make: trade name super ZORU 1500), and it prepared as a transparent coloring paint. And this transparent coloring paint was formed as the 28.5-29.5-micrometer bead adhesion layer 13B on the above-mentioned transparent coloring layer.

C. The bead (Nippon Electric Glass [ Co., Ltd. ] make: trade name SK-73) 14A with a mean particle diameter of about 73 micrometers was made to adhere to the formation (1) above-mentioned bead adhesion layer 13B of the reflective element 14.

[0020]Acrylic resin (Tokushu Shikiryō Color & Chemicals [ , INC. ] make: trade name ST-400) (2) 100 weight sections, After carrying out toluene 31.8 weight-section addition of 5.5 weight sections and the MIBK for melamine cross-linking agent NIKARAKKU MS-11 21.2 weight sections and improving this stirring mixing, it applied to a bead adhesion layer and formed as the focal layer 14B.

Rank second and acrylic resin (Tokushu Shikiryō Color & Chemicals [ , INC. ] make: trade name ST-540) (3) 100 weight sections, After carrying out 5.5 weight sections for melamine cross-linking agent MS-11 and improving 27.9 weight sections and toluene 41.9 weight section stirring mixing of the MIBK, it applied to the focal layer 14B, and formed as the focal layer 14C. The focal layer 14B and the focal layer 14C formed each by thickness that luminosity as a reflective sheet becomes the highest.

(4) On the focal layer 14C, aluminum was made to vapor-deposit and the appropriate back formed as the light reflection film 14D.

[0021]Preparation acrylic adhesives (Nippon Carbide Industries [ Co., Inc. ] make: trade name KP-1043) of the base material sheet 15 D. 100 weight sections, Ten weight sections and colorant (Tokushu Shikiryō Color & Chemicals [ , INC. ] make: trade name AR-9127) for ethyl acetate Eight weight sections, Mixed stirring was improved cross linking agent (what diluted trade name coronate L made from Japanese Polyurethane Industry with toluene to 10%) 6 weight section, it applied to a releasing paper (LINTEC [ Corp. ] make: trade name E2 P-SH), a 50-micrometer white adhesive layer was formed, and it prepared as the base material sheet 15.

[0022]E. A lamination layer sheet produced in a procedure of production above-mentioned A-C of a retroreflection sheet was pasted together to a base material sheet produced in Procedure D, and this invention article 1 was produced.

[0023]In this invention article 1 obtained in a procedure of above-mentioned A-E, total light transmittance of a transparent fluorescence coloring layer was 69.5%. Total light transmittance of a transparent coloring layer was 51.4%. Luminosity of a retroreflection sheet is 40.5 in 4 degrees of incidence angles in 0.2 degree of observation angles.

The chroma saturation is 69.7 and visibility brought a result shown in Table 1.

According to the result shown in the following table 1, it turned out that it excels in visibility also to any of the white back and the black back.

[0024]In embodiment 2. this example, this invention article 2 was produced like Embodiment 1 except [ all ] transparent fluorescence coloring layer thickness having been 23-24 micrometers. Total light transmittance of this this invention article 2 was 70.6%. Total light transmittance of a transparent coloring layer was 51.4%. A retroreflection sheet. Luminosity is 47.7 in 4 degrees of incidence angles in 0.2 degree of observation angles.

The chroma saturation is 68.8 and visibility brought a result shown in Table 1.

According to the result shown in the following table 1, it turned out that it excels in visibility also to any of the white back and the black back.

[0025]In embodiment 3. this example, 56 weight sections and fluorescence orange \*\* for fluorescence red \*\* 70 weight sections, 24.2 weight section and CT-5 for melamine cross-linking agent MS-11 6.3 weight sections, 0.6 weight sections were carried out for SHISOPU 103, stirring mixing of the MIBK was improved 30.7 weight sections, a transparent fluorescence coloring paint was prepared, and this invention article 3 was produced like Embodiment 1 except [ all ] having applied this transparent fluorescence coloring paint to a PET film, and having formed a 23-24-micrometer transparent fluorescence coloring layer. Luminosity of this this invention article 3 is 43.5 in 4 degrees of incidence angles in 0.2 degree of observation angles.

The chroma saturation is 66.3 and visibility brought a result shown in Table 1.

According to the result shown in the following table 1, it turned out that it excels in visibility also to any of the white back and the black back.

[0026]In embodiment 4. this example, this invention article 4 was produced like Embodiment 3 except [ all ] transparent fluorescence coloring layer thickness having been 20-21 micrometers. The luminosity of this this invention article 4 is 52.7 in 4 degrees of incidence angles in 0.2 degree of observation angles.

The chroma saturation is 65.1 and visibility brought a result shown in Table 1.

According to the result shown in the following table 1, it turned out that it excels in visibility somewhat conventionally also to any of the white back and the black back.

[0027]In embodiment 5. this example, this invention article 5 was produced like Embodiment 3 except [ all ] transparent fluorescence coloring layer thickness having been 18-19 micrometers. The luminosity of this this invention article 5 is 37.4 in 4 degrees of incidence angles in 0.2 degree of observation angles.

The chroma saturation is 61.3 and visibility brought a result shown in Table 1.

According to the result shown in the following table 1, it turned out that before is excelled a little in visibility also to any of the white back and the black back.

[0028]In embodiment 6. this example, acrylic resin ST-100 100 weight sections, 39.2 weight sections and fluorescence orange \*\* for fluorescence red \*\* 153.2 weight sections, 51.5 weight section and CT-5 for melamine cross-linking agent MS-11 13.5 weight sections, 1.5 weight sections were carried out for SHISOPU 103, stirring mixing of the MIBK was improved 53.8 weight sections, the transparent fluorescence coloring paint was prepared, and this invention article 6 was produced like Embodiment 4 except [ all ] having applied this transparent fluorescence coloring paint to the PET film, and having formed a 25-26-micrometer transparent fluorescence coloring layer. The luminosity of this this invention article 6 is 50.4 in 4 degrees of incidence angles in 0.2 degree of observation angles.

The chroma saturation is 61.9 and visibility brought a result shown in Table 1.

According to the result shown in the following table 1, it turned out that before is excelled a little in visibility also to any of the white back and the black back. The total light transmittance of the transparent fluorescence coloring layer of this this invention article 6 was 79.0%. The total light transmittance of the transparent coloring layer was 51.4%.

[0029]In embodiment 7. this example, this invention article 7 was produced like Embodiment 4 except having applied to a PET film a transparent fluorescence coloring paint used in Embodiment 6, and having formed a 23-24-micrometer transparent fluorescence coloring layer. Luminosity of this this invention article 7 is 42.8 in 4 degrees of incidence angles in 0.2 degree of observation angles.

The chroma saturation is 58.3 and visibility brought a result shown in Table 1.

According to the result shown in the following table 1, it turned out that before is excelled a little in visibility also to any of the white back and the black back. Total light transmittance of a transparent fluorescence coloring layer of this this invention article 7 was 79.0%. Total light transmittance of a transparent coloring layer was 51.4%.

[0030]

[Table 1]

	5 0 m	1 0 0 m	試 料	5 0 m	1 0 0 m	
白 バ ッ ク	◎	◎	本発明品 1	◎	◎	黒 バ ッ ク
	◎	◎	本発明品 2	◎	◎	
	◎	◎	本発明品 3	◎	◎	
	○	○	本発明品 4	◎	○	
	△	△	本発明品 5	○	○	
	△	△	本発明品 6	○	○	
	△	△	本発明品 7	△	△	

◎：従来の反射シートと比較して非常に視認性が良い

○：従来の反射シートと比較して視認性が良い

△：従来の反射シートと比較して多少視認性が良い

[0031]

[Effect of the Invention]The retroreflection sheet of this invention can fully be recognized visually daytime also.

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[Translation done.]